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L4   ANSWER 1 OF 3  CAPLUS  COPYRIGHT 2009 ACS on STN
AN   1999:271117  CAPLUS
DN   130:339440
ED   Entered STN:  03 May 1999
TI   Polysilazane-containing compositions and silica coatings and manufacturing
     methods therefor
IN   Aoki, Satoko; Shimizu, Yasuo; Funayama, Toru
PA   Tonen Co., Ltd., Japan
SO   Jpn. Kokai Tokkyo Koho, 18 pp.
     CODEN: JKXXAF
DT   Patent
LA   Japanese
IC   ICM  C08L083-16
     ICS  C08K005-34
CC   42-10 (Coatings, Inks, and Related Products)
     Section cross-reference(s): 58, 76
FAN.CNT 1
     PATENT NO.          KIND   DATE         APPLICATION NO.        DATE
     ---------------     ----   --------     --------------------   --------
PI   JP 11116815          A     19990427     JP 1997-285197         19971017 <--
     JP 3904691           B2    20070411
PRAI JP 1997-285197             19971017
CLASS
 PATENT NO.      CLASS  PATENT FAMILY CLASSIFICATION CODES
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 JP 11116815     ICM    C08L083-16
                 ICS    C08K005-34
                 IPCI   C09D0183-16 [I,A]
                 IPCR   C08K0005-00 [I,C*]; C08K0005-34 [I,A]; C08L0083-00
                        [I,C*]; C08L0083-16 [I,A]; C09D0183-16 [I,C];
                        C09D0183-16 [I,A]
AB   Polysilazanes or modified polysilazanes convert to silica rapidly when
     contain N heterocyclic compds.  Thus, a solution containing 20 g
     perhydropolysilazane, 1 g 1,3-di-4-piperidylpropane, and Bu2O was spin
     coated on a Si wafer and converted completely to a silica coating.
ST   perhydropolysilazane piperidylpropane coating silicon wafer; silica
     coating silicon wafer; nitrogen heterocycle catalyst perhydropolysilazane
     reaction
IT   Amines, uses
     RL: CAT (Catalyst use); USES (Uses)
        (cyclic; polysilazanes containing nitrogen heterocyclic compds. for rapid
        conversion to silica coatings)
IT   Heterocyclic compounds
     RL: CAT (Catalyst use); USES (Uses)
        (nitrogen; polysilazanes containing nitrogen heterocyclic compds. for rapid
        conversion to silica coatings)
IT   Ceramic coatings
     Oxidation catalysts
     Polymer degradation catalysts
     Polymerization
        (polysilazanes containing nitrogen heterocyclic compds. for rapid
        conversion to silica coatings)
IT   Silazanes
     RL: IMF (Industrial manufacture); RCT (Reactant); TEM (Technical or
     engineered material use); PREP (Preparation); RACT (Reactant or reagent);
     USES (Uses)
        (polysilazanes containing nitrogen heterocyclic compds. for rapid
        conversion to silica coatings)
IT   Coating process
        (spin; polysilazanes containing nitrogen heterocyclic compds. for rapid
        conversion to silica coatings)
IT   Semiconductor materials
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(wafers; polysilazanes containing nitrogen heterocyclic compds. for rapid conversion to silica coatings)

IT 280-57-9, 1,4-Diazabicyclo[2.2.2]octane 16898-52-5, 1,3-Di-4-piperidylpropane 21655-48-1, cis-2,6-Dimethylpiperazine 64168-11-2, 4,4'-Trimethylenebis(1-methylpiperidine)
RL: CAT (Catalyst use); USES (Uses)
(polysilazanes containing nitrogen heterocyclic compds. for rapid conversion to silica coatings)

IT 125571-38-2P 149013-47-8P, Perhydropolysilazane
RL: IMF (Industrial manufacture); RCT (Reactant); TEM (Technical or engineered material use); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(polysilazanes containing nitrogen heterocyclic compds. for rapid conversion to silica coatings)

IT 7631-86-9P, Silica, uses
RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(polysilazanes containing nitrogen heterocyclic compds. for rapid conversion to silica coatings)

IT 7440-21-3, Silicon, uses
RL: DEV (Device component use); USES (Uses)
(wafers; polysilazanes containing nitrogen heterocyclic compds. for rapid conversion to silica coatings)

OSC.G 2 THERE ARE 2 CAPLUS RECORDS THAT CITE THIS RECORD (2 CITINGS)
UPOS.G Date last citing reference entered STN: 16 Feb 2009
OS.G CAPLUS 2002:849751; 2001:453173
RN 280-57-9
RN 16898-52-5
RN 21655-48-1
RN 64168-11-2
RN 125571-38-2P
RN 149013-47-8P
RN 7631-86-9P
RN 7440-21-3

L4 ANSWER 2 OF 3 WPIX COPYRIGHT 2009 THOMSON REUTERS on STN
AN 1999-323713 [27] WPIX
DNC C1999-095646 [27]
TI Poly-silazane composition for preparation of silica membrane - comprises optionally modified poly-silazane and nitrogen-containing heterocyclic compound
DC A26; A85; E36; L02; L03
IN AOKI T; FUNAYAMA T; SHIMIZU Y
PA (TOFU-C) TONEN CORP; (AZEL-N) AZ ELECTRONIC MATERIALS KK
CYC 1
PI JP 11116815 A 19990427 (199927)* JA 18[13] <--
JP 3904691 B2 20070411 (200726) JA 22
ADT JP 11116815 A JP 1997-285197 19971017; JP 3904691 B2 JP 1997-285197 19971017
FDT JP 3904691 B2 Previous Publ JP 11116815 A
PRAI JP 1997-285197 19971017
IPCI C09D0183-16 [I,A]; C09D0183-16 [I,C]
IPCR C08K0005-00 [I,C]; C08K0005-34 [I,A]; C08L0083-00 [I,C]; C08L0083-16 [I,A]
FCL C08K0005-34; C08L0083-16; C09D0183-16
FTRM 4J002; 4J038; 4J002/CP21.1; 4J002/EU02.6; 4J002/EU04.6; 4J002/EU07.6; 4J002/EU09.6; 4J002/EU11.6; 4J002/EU13.6; 4J002/EU18.6; 4J002/GH01; 4J002/GQ01; 4J002/GQ05

AB JP 11116815 A UPAB: 20050704
Poly-silazane composition (I) comprising (A) and (B) is claimed. (A) is optionally modified poly-silazane having repeat units of formula (1) and Mn 100- 50,000. (B) is nitrogen-containing heterocyclic compound.
-(-SiR1R2-NR3-)- (1)
R1, R2, R3 = H, alkyl, alkenyl, cycloalkyl, aryl, alkylsilyl, alkylamino, alkoxy having carbon atom(s) binding to silicone atom(s).

Preparation of silica membrane from (I) membrane is also claimed.
USE - (I) is useful as material for preparation of insulating membrane, flatting membrane etc for semiconductor devices, liquid crystal devices etc.
ADVANTAGE - Membrane of (I) can be converted to silica membrane at 25-100 °C, (I) gives silica membrane having good insulating properties, resistance to heat, abrasion, corrosion etc.
MC CPI: A06-A00E2; A06-A00E4; A10-E05; A12-E07C; A12-L03B; E31-P01; L02-G07; L02-G12; L03-D01
AN 1999-323713 [27] WPIX
DNC C1999-095646 [27]
TI Poly-silazane composition for preparation of silica membrane - comprises optionally modified poly-silazane and nitrogen-containing heterocyclic compound
DC A26; A85; E36; L02; L03
IN AOKI T; FUNAYAMA T; SHIMIZU Y
PA (TOFU-C) TONEN CORP; (AZEL-N) AZ ELECTRONIC MATERIALS KK
CYC 1
PI JP 11116815 A 19990427 (199927)* JA 18[13] <--
JP 3904691 B2 20070411 (200726) JA 22
ADT JP 11116815 A JP 1997-285197 19971017; JP 3904691 B2 JP 1997-285197 19971017
FDT JP 3904691 B2 Previous Publ JP 11116815 A
PRAI JP 1997-285197 19971017
IPCI C09D0183-16 [I,A]; C09D0183-16 [I,C]
IPCR C08K0005-00 [I,C]; C08K0005-34 [I,A]; C08L0083-00 [I,C]; C08L0083-16 [I,A]
FCL C08K0005-34; C08L0083-16; C09D0183-16
FTRM 4J002; 4J038; 4J002/CP21.1; 4J002/EU02.6; 4J002/EU04.6; 4J002/EU07.6; 4J002/EU09.6; 4J002/EU11.6; 4J002/EU13.6; 4J002/EU18.6; 4J002/GH01; 4J002/GQ01; 4J002/GQ05
AB JP 11116815 A UPAB: 20050704
Poly-silazane composition (I) comprising (A) and (B) is claimed. (A) is optionally modified poly-silazane having repeat units of formula (1) and Mn 100- 50,000. (B) is nitrogen-containing heterocyclic compound.
-(-SiR1R2-NR3-)- (1)
R1, R2, R3 = H, alkyl, alkenyl, cycloalkyl, aryl, alkylsilyl, alkylamino, alkoxy having carbon atom(s) binding to silicone atom(s).
Preparation of silica membrane from (I) membrane is also claimed.
USE - (I) is useful as material for preparation of insulating membrane, flatting membrane etc for semiconductor devices, liquid crystal devices etc.
ADVANTAGE - Membrane of (I) can be converted to silica membrane at 25-100 °C, (I) gives silica membrane having good insulating properties, resistance to heat, abrasion, corrosion etc.
ABDT JP11116815
Poly-silazane composition (I) comprising (A) and (B) is claimed. (A) is optionally modified poly-silazane having repeat units of formula (1) and Mn 100- 50,000. (B) is nitrogen-containing heterocyclic compound.
-(-SiR1R2-NR3-)- (1)
R1, R2, R3 = H, alkyl, alkenyl, cycloalkyl, aryl, alkylsilyl, alkylamino, alkoxy having carbon atom(s) binding to silicone atom(s).
Preparation of silica membrane from (I) membrane is also claimed.
USE
(I) is useful as material for preparation of insulating membrane, flatting membrane etc for semiconductor devices, liquid crystal devices etc.
ADVANTAGE
Membrane of (I) can be converted to silica membrane at 25-100 °C,
(I) gives silica membrane having good insulating properties, resistance to heat, abrasion, corrosion etc.
EXAMPLE
A mixture of 1,3-di(4-piperidyl)propane 1.0 g and dibutyl ether 30 g was added to a mixture of per-hydro-poly-silazane (Mn 800) 20 g and dibutyl ether 50 g dropwise over 5 minutes to obtain (I) dibutyl ether solution. The solution was cast on silicon wafer to form (I) membrane which was held

at 90 °C under relative humidity 80 % atmosphere for 10 min. The (I) membrane was converted to silica membrane completely.
EMBODIMENT
(A) is per-hydro-poly-silazane having structure of formula (6) or (7). (B) is one or more of 1,3-di(4-piperidyl)propane, 4,4'-trimethylenebis(1-methylpiperidine), diazabicyclo[2,2,2]octane or cis 2,6-dimethylpiperazine. (I) is prepared by blending (A) 100 pts wt, (B) 0.1-10 pts wt and opt. additive(s)(e.g. plasticiser, antistatic agent, filler, solvent etc) at 0-200 °C under 0 - 9.8 + 105 Pa.

FS CPI

MC CPI: A06-A00E2; A06-A00E4; A10-E05; A12-E07C; A12-L03B; E31-P01; L02-G07; L02-G12; L03-D01

L4 ANSWER 3 OF 3 JAPIO (C) 2009 JPO on STN

AN 1999-116815 JAPIO

TI POLYSILAZANE-CONTAINING COMPOSITION AND FORMATION OF SILICEOUS FILM

IN AOKI TOMOKO; SHIMIZU YASUO; FUNAYAMA TORU

PA TONEN CORP

PI JP 11116815 A 19990427 Heisei

AI JP 1997-285197 (JP09285197 Heisei) 19971017

PRAI JP 1997-285197 19971017

SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1999

IC ICM C08L083-16
ICS C08K005-34

AB PROBLEM TO BE SOLVED: To obtain the subject composition having high silica-conversion rate and capable of converting a polysilazane thin film into a siliceous film even under ambient condition having low relative humidity by including a (modified) polysilazane containing a specific skeleton and an N-heterocyclic compound.
SOLUTION: The objective composition contains a polysilazane or its modified product containing the skeleton of the formula (R<SP>1</SP> to R<SP>3</SP> are each H, an alkyl, an aryl or the like; at least one of R<SP>1</SP> and R<SP>2</SP> is H) as a main skeleton and having a number-average molecular weight of 1,000-50,000 and an N-heterocyclic compound. A siliceous film can be formed by forming a coating film of the composition and leaving under ambient condition or heating the coating film.

=>

10/591573

PTO 08-6949

CC=JP
DATE=19990427
KIND=A
PN=11116815

POLYSILAZANE-CONTAINING COMPOSITION AND METHOD FOR FORMING SILICEOUS FILM
[ポリシラザン含有組成物及びシリカ質膜の形成方法]

TOMOKO AOKI ET AL.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. AUGUST 2008

TRANSLATED BY SCHREIBER TRANSLATIONS, INC.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	11116815
DOCUMENT KIND	(12):	A
PUBLICATION DATE	(43):	19990427
APPLICATION NUMBER	(21):	09285197
APPLICATION DATE	(22):	19971017
INTERNATIONAL CLASSIFICATION	(51):	C08L 83/16, C08K 5/34
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTOR(S)	(72):	TOMOKO AOKI, YASUO SHIMIZU, TORU FUNAYAMA
APPLICANT(S)	(71):	TONEN CORP.
DESIGNATED CONTRACTING STATES	(81):	
TITLE	(54):	POLYSILAZANE-CONTAINING COMPOSITION AND METHOD FOR FORMING SILICEOUS FILM
FOREIGN TITLE	[54A]:	ポリシラザン含有組成物及びシリカ質膜の形成方法

[Claims] /2[1]

[Claim 1] A polysilazane-containing composition primarily comprising a polysilazane having a number average molecular weight of 100 to 50,000 containing the skeleton denoted by general formula (I) below:

[Chem. 1]


(I)

(wherein each of R^1, R^2, and R^3 independently denotes a hydrogen atom, alkyl group, alkenyl group, cycloalkyl group, aryl group, some other group in which the portion directly bonded to the silicon is carbon, alkylsilyl group, alkylamino group, or alkoxy group, with at least one from among R^1 and R^2 denoting a hydrogen atom), or a modified product thereof, and an N-heterocyclic compound.

[Claim 2] A method for forming a siliceous film characterized by the steps of:

forming a coating of a polysilazane-containing composition primarily comprising a polysilazane having a number average molecular weight of 100 to 50,000 containing the skeleton denoted by general formula (I) below:

[Chem. 2]

[1] Numbers in the margin indicate pagination in the foreign text.

(I)

(wherein each of R^1, R^2, and R^3 independently denotes a hydrogen atom, alkyl group, alkenyl group, cycloalkyl group, aryl group, some other group in which the portion directly bonded to the silicon is carbon, alkylsilyl group, alkylamino group, or alkoxy group, with at least one from among R^1 and R^2 denoting a hydrogen atom), or a modified product thereof, and an N-heterocyclic compound; and

allowing said coating to stand under ambient conditions or heating said coating.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to polysilazane-containing compositions, and more particularly, to a composition containing a specific compound for increasing the rate of conversion to silica, and to a method for forming a siliceous film.

[0002]

[Prior Art] Siliceous films are employed in a variety of technical fields as coatings affording good heat resistance, abrasion resistance, corrosion resistance, insulating properties, and the like. Known methods of forming

siliceous films include PVD, CVD, the sol-gel method, and various methods based on coating materials. However, in recent years, a method affording greater advantages than these methods in terms of processing, cost, and film quality has been developed in which a precursor polymer of polysilazane or the like is coated and baked.

[0003] A dense, high-purity silica film can be obtained by baking a thin film of polysilazane in air, but a baking temperature of about 400°C or higher is required. The present applicants have developed a low-temperature ceramic-forming polysilazane composition containing various additives, described further below, that are necessary to lower the heating temperature required for the conversion of polysilazane to silica. Additionally, as is described in Japanese Patent Application Publication Heisei No. 9-31333, the present applicants have achieved a lower temperature and a higher rate in the silica conversion step through contact with an amine and/or an acid.

[0004]

[Problem to Be Solved by the Invention] According to Japanese Patent Application Publication Heisei No. 9-31333, converting amine-containing polysilazane to silica at a low temperature requires contacting the polysilazane with an equivalent quantity of water. Generally, high purity is

required when employing a siliceous film as an insulating film, smoothing film, or the like in a semiconductor device or liquid crystal device. However, to convert a polysilazane thin film to a desired high-purity siliceous film requires the use of high-temperature, highly humid atmosphere (particularly a highly humid environment of 200°C or higher) even when employing the method described in the above-cited publication. However, such temperature and high humidity are problematic in that they negatively affect the characteristics of semiconductor devices and the like. Accordingly, it is desirable to be able to convert a polysilazane thin film to a high-purity siliceous film under conditions of lower humidity, desirably in a dry atmosphere.

[0005] Further, polysilazane has a broad molecular weight distribution ranging from several hundred to several tens of thousands. Thus, the low molecular weight components reach their boiling points in the course of heating a polysilazane thin film, scattering as vapor. The vapor adheres to the interior of the heating apparatus, becoming a source of contamination of the finished product or heating apparatus. Scattering of low-boiling components also diminishes the conversion yield (film yield) of polysilazane to silica. Accordingly, it is desirable to

minimize vapor generation of low-molecular-weight components in the course of heating the polysilazane thin film to both prevent contamination of the heating apparatus and the like and enhance the yield of siliceous film.

[0006]

/3

[Means of Solving the Problem] The present inventors conducted extensive research, resulting in the discovery that when an N-heterocyclic compound was added to a polysilazane composition, polysilazane thin films were unexpectedly converted to siliceous films at high film yields in an atmosphere of relatively low humidity, such as air, and in some cases, even in dry atmospheres. The present invention was devised on this basis. That is, the present invention provides:

(1) a polysilazane-containing composition primarily comprising a polysilazane having a number average molecular weight of 100 to 50,000 containing the skeleton denoted by general formula (I) below:

[0007]

[Chem. 3]

(I)

[0008] (wherein each of R^1, R^2, and R^3 independently denotes a hydrogen atom, alkyl group, alkenyl group, cycloalkyl group, aryl group, some other group in which the portion directly bonded to the silicon is carbon, alkylsilyl group, alkylamino group, or alkoxy group, with at least one from among R^1 and R^2 denoting a hydrogen atom), or a modified product thereof, and an N-heterocyclic compound; and

(2) a method for forming a siliceous film characterized by the steps of:

forming a coating of a polysilazane-containing composition primarily comprising a polysilazane having a number average molecular weight of 100 to 50,000 containing the skeleton denoted by general formula (I) below:

[0009]

[Chem. 4]

(I)

[0010] (wherein each of R^1, R^2, and R^3 independently denotes a hydrogen atom, alkyl group, alkenyl group, cycloalkyl group, aryl group, some other group in which the portion directly bonded to the silicon is carbon, alkylsilyl group, alkylamino group, or alkoxy group, with at least one from among R^1 and R^2 denoting a hydrogen atom), or a modified

product thereof, and an N-heterocyclic compound; and allowing said coating to stand under ambient conditions or heating said coating.

[0011] Examples of desirable implementation modes of the present invention are given below:

(3) The polysilazane-containing composition of (1) above, wherein said polysilazane is perhydropolysilazane;

(4) The polysilazane-containing composition of (1) or (3) wherein said N-heterocyclic compound does not exhibit aromatic properties;

(5) The polysilazane-containing composition of (4), wherein said N-heterocyclic compound is at least one compound selected from the group consisting of 1,3-di-4-piperidylpropane, 4,4'-triemthylenebis(1-methylpiperidine), diazabicyclo[2.2.2]octane, and cis-2,6-dimethylpiperazine;

(6) The polysilazane-containing composition of any one of (1) and (3) to (5), wherein said N-heterocyclic compound is incorporated in a quantity of 0.1 to 10 weight percent of the polysilazane;

[0012] (7) The method of (2), further characterized in that said heating is conducted under humidified conditions;

(8) The method of (2), further characterized in that said heating is divided into a step of prebaking at 200°C or lower at a relative humidity of 30 percent or higher,

followed by a main baking step of heating at 200°C or higher at a relative humidity of 30 percent or lower;

(9) The method of (8) wherein the relative humidity in said main baking step is 20 percent or lower;

(10) The method of (8) wherein the relative humidity in said main baking step is 10 percent or lower;

(11) The method of (8) wherein the relative humidity in said main baking step is essentially 0 percent; and

(12) The method of any one of (8) to (11), further characterized in that the relative humidity in said prebaking step is 40 percent or lower.

[0013] Adding an N-heterocyclic compound to the polysilazane composition in the present invention greatly increases the silica conversion rate relative to poly-silazane alone or to conventional polysilazane compositions (particularly those to which aliphatic amines are added), and it becomes possible to convert polysilazane thin films to siliceous films under conditions of low relative humidity, sometimes even in a dry atmosphere. Thus, the high-temperature, high-humidity atmospheres that present the risk of negatively affecting device characteristics can be avoided when employing polysilazane-derived siliceous films as insulating layers and smoothing layers in semiconductor devices and liquid-crystal devices. Further,

the high rate of conversion to silica increases the ratio of conversion to high molecular weight prior to low-molecular-weight components of polysilazane reaching their boiling points during heating and vaporizing. Thus, the vaporization of low-molecular-weight components is reduced in the course of heating the polysiloxane thin film, and contamination of the heating apparatus and the like is prevented, enhancing the yield of siliceous film due to the reduction in the amount of vapor scattering.

/4

[0014] The present invention is described in greater detail below. The polysilazane employed in the present invention need only comprise at least an intramolecular Si-H bond or N-H bond. Polysilazane alone, copolymers of polysilazane and other polymers, and mixtures of polysilazane and other compounds can be employed. The polysilazane employed may have a chainlike, cyclic, or crosslinked structure, and multiple such structures may be simultaneously present within the molecule. These polysilazanes may be employed singly or as mixtures.

[0015] Representative examples of the polysilazane employed are given below. However, the polysilazane is not limited thereto. Perhydropolysilazane is desirable from the perspectives of the hardness and density of the film

obtained, while organopolysilazanes are desirable from the perspective of flexibility. The polysilazane may be suitably selected in accordance with the application by one of ordinary skill in the art. When R^1, R^2, and R^3 denote hydrogen atoms, general formula (I) above denotes perhydropolysilazane. By way of example, the manufacturing methods reported in Japanese Patent Application Publication Showa No. 63-16325 and D. Seyferth et al., Communication of Am. Cer. Soc., C-13, January 1983 can be employed. These methods yield mixtures of polymers having various structures. However, they basically comprise intramolecular chainlike component and cyclic components that can be represented by the chemical formulas:

[0016]

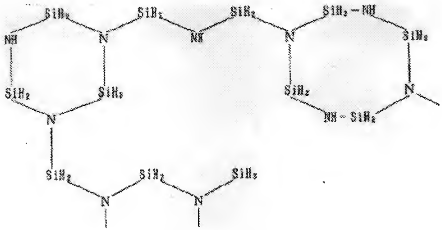
[Chem. 5]

$$-\!\!\left(SiH_2NH \right)_a\!\!- \quad -\!\!\left(SiH_2N \right)_b\!\!< \quad -\!\!\left(SiH_3 \right)_c \quad (a+b+c=1)$$

[0017] An example of the structure of perhydropolysilazane is given below:

[0018]

[Chem. 6]



[0019] A method of manufacturing a polysilazane in which R^1 and R^2 denote hydrogen atoms and R^3 denotes a methyl group in general formula (I) is reported in D. Seyferth et al., Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 25, 10 (1984). The polysilazane obtained by this method comprises repeating units in the form of a $-(SiH_2NCH_3)-$ chainlike polymer and a cyclic polymer, neither of which have a crosslinked structure. Methods of manufacturing polyorgano(hydro)silazanes in which R^1 and R^3 denote hydrogen atoms and R^2 denotes an organic group in general formula (I) are reported in D. Seyferth et al., Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 25, 10 (1984), and Japanese Patent Application Publication Showa Nos. 61-89230 and 62-156135. The polysilazanes obtained by these methods include those having a cyclic structure with a degree of polymerization of primarily 3 to 5 with a repeating unit in the form of $-(R^2SiHNH)-$, and those

simultaneously comprising intramolecular chainlike structures and cyclic structures, denoted by the chemical formula $(R^3 SiHNH)_x ((R^2SiH)_{1.5}N)_{1-x}$ $(0.4 < x < 1)$.

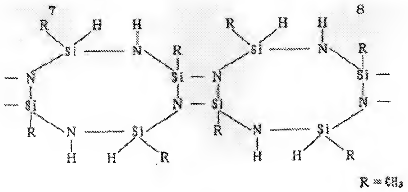
[0020] Polysilazanes in which R^1 denotes a hydrogen atom and R^2 and R^3 denote organic groups in general formula (I), and polysilazanes in which R^1 and R^2 denote organic groups and R^3 denotes a hydrogen atom, have a cyclic structure with a repeating unit in the form of $-(R^1R^2SiNR^3)-$ and a degree of polymerization of primarily 3 to 5. The polysilazane employed has a main skeleton comprised of the unit denoted by general formula (I) above. However, the unit denoted by general formula (I) is sometimes cyclized in the manner clearly indicated above. In such cases, the cyclic portion becomes a terminal group. When such cyclization is not present, the terminal of the main skeleton can be a group identical to R^1, R^2, or R^3, or hydrogen.

[0021] There are also polyorgano(hydro)silazanes having an intramolecular crosslinked structure such as that reported by D. Seyferth et al., Communication of Am. Cer. Soc., C-132, July 1984. An example is given below:

[0022]

[Chem. 7]

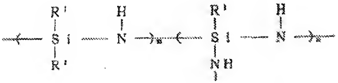
/5



[0023] Further, polysilazanes ($R^1Si(NH)_x$) such as those reported in Japanese Patent Application Publication Showa No. 49-69717, which have a crosslinked structure obtained by R^1SiX_3 (X: halogen) ammonia degradation, and polysilazanes having the following structure obtained by ammonia codegradation of R^1SiX_3 and $R^2{}_2SiX_2$, can be employed as starting materials.

[0024]

[Chem. 8]



(m, n: positive integers)

[0025] A polymetallosilazane comprising a metal atom, such as in the following structure (wherein M on the metal atom side chain optionally forms a crosslink), can also be employed as a starting material.

[0026]

[Chem. 9]

(m, n: positive integers)

(M is a metal atom)

[0027] Additionally, polysiloxazanes with repeating units denoted by $((SiH_2)_n(NH)_m)$ and $((SiH_2)_xO)$ (wherein each of n, m, and r denotes 1, 2, or 3), such as those reported in Japanese Patent Application Publication Showa No. 62-195024; polyborosilazanes affording good heat resistance manufactured by reacting a boron compound with a polysilazane, such as those reported in Japanese Patent Application Publication Heisei No. 2-84437; polymetallosilazanes manufactured by reacting a polysilazane with metal alkoxide, such as those reported in Japanese Patent Application Publication Showa Nos. 63-81122 and 63-191832, and Japanese Patent Application Publication Heisei No. 2-77427; inorganic silazane high polymers and modified polysilazanes with increased molecular weight such as those reported in Japanese Patent Application Publication Heisei Nos. 1-138108, 1-138107, 1-203429, and 1-203430, and with enhanced resistance to hydrolysis such as those reported in Japanese Patent Application Publication Heisei Nos. 4-63833 and 3-320167; and copolymer

polysilazanes that are advantageous for thick films in which organic components are incorporated into polysilazanes, such as those reported in Japanese Patent Application Publication Heisei Nos. 2-175726, 5-86200, 5-331293, and 3-31326; and the like can be employed.

[0028] Low-temperature ceramic-forming polysilazanes such as those set forth below can also be employed in the present invention. One example is the silicon alkoxide-added polysilazane described in Japanese Patent Application Publication Heisei No. 5-238827 by the present applicants. This modified polysilazane is obtained by hot reacting the polysilazane denoted by general formula (I) above and the silicon alkoxide denoted by general formula (II) below:

$$Si(OR^4) \qquad \text{(II)}$$

(wherein each of the multiple instances of R^4, which may be identical or different, denotes a hydrogen atom, alkyl group having 1 to 20 carbon atoms, or aryl group, with at least one instance of R^4 denoting the above-described alkyl group or aryl group). It is a silicon alkoxide-added poly-silazane in which the atomic ratio of alkoxide-derived silicon/polysilazane-derived silicon ranges from 0.001 to 3 and the number average molecular weight is about 200 to 500,000. R^4 desirably denotes an alkyl group having 1 to 10 carbon atoms, preferably an alkyl group having 1 to 4

carbon atoms. Further, the atomic ratio of alkoxide-derived silicon to polysilazane-derived silicon desirably falls within a range of 0.05 to 2.5. See Japanese Patent Application Publication Heisei No. 5-238827 for how to prepare silicon alkoxide-added polysilazane.

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[0029] A further example of a low-temperature ceramic-forming polysilazane is the glycidol-added polysilazane described in Japanese Patent Application Publication Heisei No. 6-122852 of the present applicants. This modified polysilazane is obtained by reacting a polysilazane denoted by general formula (I) above with glycidol. In this glycidol-added polysilazane, the glycidol/polysilazane weight ratio ranges from 0.001 to 2 and the number average molecular weight is about 200 to 500,000. The glycidol/polysilazane weight ratio is desirably 0.01 to 1, preferably 0.05 to 0.5. See Japanese Patent Application Publication Heisei No. 6-122852 for how to prepare this glycidol-added polysilazane.

[0030] A still further example of a low-temperature ceramic-forming polysilazane is the alcohol-added polysilazane described in Japanese Patent Application Publication Heisei No. 6-240208 of the present applicants. This modified polysilazane is an alcohol-added polysilazane

obtained by reacting a polysilazane denoted by general formula (I) above with an alcohol, has an alcohol/polysilazane weight ratio ranging from 0.001 to 2, and has a number average molecular weight of about 100 to 500,000. The alcohol is desirably one having a boiling point of 110°C or higher, such as methanol, hexanol, octanol, nonanol, methoxyethanol, ethoxyethanol, or furfuryl alcohol. The alcohol/polysilazane weight ratio is desirably 0.01 to 1, preferably 0.05 to 0.5. See Japanese Patent Application Publication Heisei No. 6-240208 for how to prepare this alcohol-added polysiloxane.

[0031] A still further example of a low-temperature ceramic-forming polysilazane is the metal carboxylate-added polysilazane described in Japanese Patent Application Publication Heisei No. 6-299118 of the present applicants. This modified polysilazane is obtained by reacting a polysilazane of general formula (I) above with at least one metal selected from the group consisting of nickel, titanium, platinum, rhodium, cobalt, iron, ruthenium, osmium, palladium, iridium, and aluminum. It is a metal carboxylate-adduct polysilazane with a metal carboxylate/polysilazane weight ratio ranging from 0.000001 to 2 and a number average molecular weight of about 200 to 500,000. The metal carboxylate is a compound denoted by

the formula $(RCOO)_nM$ (wherein R denotes an aliphatic group having 1 to 22 carbon atoms or an alicyclic group, M denotes at least one metal selected from the above group, and n denotes the valence of metal M). The metal carboxylate may be an anhydride or a hydrate. The metal carboxylate/polysilazane weight ratio is desirably 0.001 to 1, preferably 0.01 to 0.5. See Japanese Patent Application Publication Heisei No. 6-299118 for how to prepare the metal carboxylate-added polysilazane.

[0032] A still further example of a low-temperature ceramic-forming polysilazane is the acetyl acetonate complex-added polysilazane described in Japanese Patent Application Publication Heisei No. 6-306329 of the present applicants. This modified polysilazane is obtained by reacting a polysilazane denoted by general formula (I) above with an acetyl acetonate complex comprising a metal in the form of nickel, platinum, palladium, or aluminum. This metal-comprising acetyl acetonate complex is a complex in which an anion $acac^-$ produced by acid dissociation from acetyl acetone(2,4-pentadione) is coordinated to a metal atom, and is general denoted by the equation $(CH_3 \cdot COCHCOCH_3)_nM$ (wherein M denotes a metal of valence n). The acetyl acetonate complex/polysilazane weight ratio is desirably 0.001 to 1, preferably 0.01 to 0.5. See Japanese

Patent Application Publication Heisei No. 6-306329 for how to prepare the acetyl acetonate complex-added polysilazane.

[0033] A still further example of a low-temperature ceramic-forming polysilazane is the metal microparticle-added polysilazane described in Japanese Patent Application Publication Heisei No. 7-196986 of the present applicants. This modified polysilazane is obtained by adding metal microparticles such as Au, Ag, Pd, or Ni to a coating solution comprising a main component in the form of the polysilazane denoted by general formula (I) above. The metal is desirably Ag. The particle diameter of the metal microparticles is desirably smaller than 0.5 μm, preferably 0.1 μm or lower, and more preferably, 0.05 μm or lower. A coating solution in which independently dispersed ultraminute particles of 0.005 to 0.01 μm in diameter are dispersed in a high-boiling-point alcohol is particularly desirable. The quantity of metal microparticles added is 0.01 to 10 weight parts, desirably 0.05 to 5 weight parts, per 100 weight parts of polysilazane. See Japanese Patent Application Publication Heisei No. 7-196986 for how to prepare the metal microparticle-added polysilazane.

[0034] As set forth above, the polysilazane-containing composition of the present invention comprises an N-heterocyclic compound. The N-heterocyclic compound in the

present invention has a catalytic effect in promoting the reaction converting the Si-N bonds of polysilazane into the Si-O bonds of silica. The term "N-heterocyclic compound" means a heterocyclic compound having at least one nitrogen atom as a hetero atom in a ring structure; such compounds generally have the above-stated catalytic effect. However, to strengthen this catalytic effect, it is desirable to employ an N-heterocyclic compound that does not exhibit aromatic properties. N-heterocyclic compounds that do not exhibit aromatic properties have a high electron density of independent electron pairs on the nitrogen atom. This is thought to contribute to further strengthening of the above catalytic effect. Since the independent electron pairs of the N-heterocyclic compound are oriented stereochemically toward the exterior, the fact that they approach the Si atoms of the polysilazane more readily than aliphatic amines in the course of the conversion reaction is also thought to contribute to strengthening the above catalytic effect.

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[0035] Specific examples of N-heterocyclic compounds that are useful in the present invention are: piperidine, piperazine, pyrrolidine, imidazolidine, pyrazolidine, pyrazoline, pyroline, pyrazine, indole, imidazole, triazine,

1,4-diazabicyclo[2,2,2]octane, 7-azabicyclo[2.2.1]heptane, and other hetero crosslinked cyclic compounds; 1,3-di-4-piperidylpropane, 4,4'-trimethylenebis(1-methylpiperidine), 2,2-dipyridylamine, and other ring-assemblage heterocyclic compounds. Examples of preferred N-heterocyclic compounds in the present invention are: 1,3-di-4-piperidylpropane, 4,4'-trimethylenebis(1-methylpiperidine), diazabicyclo-[2.2.2]octane, and cis-2,6-dimethylpiperazine.

[0036] Depending on the compound and the application, the polysilazane-containing composition of the present invention contains the above-described N-heterocyclic compound in a quantity of 0.01 to 50 weight percent of the polysilazane. Generally, as the content of the N-heterocyclic compound increases, the effect on promoting silica conversion increases. At the same time, however, there are also marked disadvantages in that the density of the siliceous film following conversion decreases, the stability of the polysilazane decreases, the handling properties of the composition deteriorate, and the like. Thus, an upper limit to the content of the N-heterocyclic compound is necessarily established based on the objective of the composition. The N-heterocyclic compound is desirably incorporated in a quantity of 0.1 to 10 weight percent of the polysilazane.

[0037] In preparing the polysilazane-containing composition of the present invention, the N-heterocyclic compound can be added to the polysilazane. The two are desirably uniformly mixed. To that end, the polysilazane and the N-heterocyclic compound are desirably mixed while being thoroughly stirred, or mixed after being individually dissolved and diluted in solvents, described further below. In particular, in the course of mixing, when the N-heterocyclic compound is a solid, it is desirably dissolved in a solvent prior to mixing. The temperature and pressure during mixing are not specifically limited; it generally suffices to conduct mixing at a temperature ranging from 0 to 200°C and a pressure ranging from 0 to 9.8×10^5 Pa (0 to 10 kg/cm^2) (gage pressure).

[0038] An ambient atmosphere of air or the like can generally be employed as the atmosphere during mixing. However, particularly when not employing a solvent or the like, it is desirable to employ a dried, inert atmosphere (such as a dry nitrogen atmosphere) to avoid increasing the weight of the polysilazane prior to use.

[0039] When employing a solvent, examples of solvents that are desirably employed are: benzene, toluene, xylene, ethylbenzene, diethylbenzene, trimethylbenzene, triethylbenzene, and other aromatic compounds; cyclohexane;

cyclohexene; decahydronaphthalene; dipentene; n-pentane, i-pentane, n-hexane, i-octane, n-nonane, i-nonane, n-decane, i-decane, and other saturated hydrocarbon compounds; ethylcyclohexane; methylcyclohexane; p-menthane; dipropyl ether, dibutyl ether, and other ethers; and methyl isobutyl ketone (MIBK) and other ketones. When employing these solvents, two or more solvents may be mixed to adjust the solubility of the polysilazane and the evaporation rate of the solvent. Further, some base materials, such as polycarbonates, are corroded by specific solvents. In such cases, a solvent that does not negatively affect the base material can be suitably selected.

[0040] The quantity (ratio) of solvent employed is selected to improve handling properties based on the coating method being employed, and will vary with the average molecular weight and molecular weight distribution of the polysilazane employed. Thus, it can be suitably admixed as desired. However, when the stability of the polysilazane and manufacturing efficiency are taken into account, the concentration of the polysilazane is 0.1 to 50 weight percent, and desirably 1 to 10 weight percent.

[0041] Suitable fillers and/or extenders can be added as needed to the polysilazane-containing composition of the present invention. Examples of fillers are micropowders of

silica, alumina, zirconia, mica, and other oxide-based inorganic compounds, and nonoxide-based inorganic compounds such as silicon carbide and silicon nitride. Depending on the application, metal powders of aluminum, zinc, copper, and the like can be added. These fillers may be acicular (including whiskers), granular, scale-shaped, or the like in shape, and may be employed singly or in mixtures of two or more. The particles of these fillers are desirably smaller in size than the thickness of the film that can be applied in a single application. The quantity of filler added ranges from 0.05 to 10 weight parts, and preferably ranges from 0.2 to 3 weight parts, per weight part of polysilazane. Various pigments, leveling agents, defoaming agents, antistatic agents, UV-absorbing agents, pH adjusting agents, dispersing agents, surface-modifying agents, plasticizers, drying enhancers, and antisagging agents can also be added to the polysilazane-containing composition.

[0042] The present invention provides a method for forming a siliceous film, characterized by comprising the steps of forming a coating of a polysilazane-containing composition containing a polysilazane such as those set forth above, or a modified product thereof, and an N-heterocyclic compound,

and allowing the coating to stand under ambient conditions or heating the coating.

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[0043] The polysilazane-containing composition of the present invention can be converted to silica in air at a temperature of about 100°C for 5 minutes or more, or at close to room temperature (about 25°C) for 30 minutes or more. Accordingly, a coating of the polysilazane-containing composition of the present invention can be formed efficiently using a metal material, inorganic material, or some other heat-resistant material, or a material with little resistance to heat, such as glass, plastic, wood, paper, or the like, as the base material (substrate). Above all, since the polysilazane-containing composition of the present invention does not require high temperature and high humidity (particularly a humidified atmosphere of 200°C or higher) for conversion to silica, there is no risk of compromising device characteristics with hot steam during conversion to silica, which is particularly advantageous, when employed as an insulating film or smoothing film in electronic devices such as semiconductors and liquid-crystals.

[0044] Common coating methods such as immersion, roll coating, bar coating, brush coating, spray coating, flow

coating, and spin coating can be employed as the means of applying the polysilazane-containing composition. When the base material is surface processed to remove filings, degreased, subjected to various forms of blasting, or the like prior to coating, adhesion of the coating is enhanced. A coating of desired thickness can be achieved by one or more repeated applications as needed. The desired film thickness will vary with the application, but as a yardstick, is 0.1 to 3 µm for semiconductor interlayer insulating films, 0.05 to 3 µm for protective films on liquid-crystal color filters, and 0.05 to 3 µm for gas barrier coatings on plastic films, for example.

[0045] Following application, the coating is dried as needed, the solvent is removed, and the coating is generally left standing under ambient conditions or heated to form a siliceous film. When the coating is left standing under ambient conditions, the polysilazane will generally adequately convert to silica after standing for 1 to 14 days, desirably 3 to 10 days. When heated, the heating temperature can be determined as desired by taking the heat-resistance temperature of the base material into account. The rate of conversion to silica is generally promoted by a heating temperature of room temperature or higher, desirably 150°C or higher. The heating means is

not specifically limited; any heating means generally employed to bake ceramics will suffice. Examples are hot plates and sintering furnaces.

[0046] The polysilazane-containing compound of the present invention attains a rate of silica conversion that is higher than in prior art even when left standing under the conditions of higher relative humidity than ambient conditions that correspond to conventional silica conversion conditions. Accordingly, subjecting the polysilazane-containing composition of the present invention to conversion to silica under conditions of high humidity yields a siliceous film at a lower temperature than in prior art, with better efficiency, and without the drawback of evaporation of low-molecular-weight components. For example, humidification to a relative humidity of 70 percent or higher, desirably 75 percent or higher, and preferably, 80 percent or higher, yields a higher rate of conversion to silicon than in prior art. That is, since the rate of conversion to silicon of the silazane-containing composition of the present invention is high, the low-molecular-weight components rapidly develop into high-molecular-weight components during baking to form a siliceous film following coating, without the generation of polysilazane vapor during baking. Thus, the yield of the

silica thin film that is obtained is good. Further, since no polysilazane vapor is generated, the various problems that are caused by such vapors are avoided.

[0047] To obtain a high-purity siliceous film of particularly good density for electronic devices such as semiconductor devices based on the present invention, since such devices undergo a loss of device characteristics when exposed to a highly moist atmosphere at an elevated temperature of 200°C or higher, the heating is desirably divided into a prebaking step in which heating is conducted at 200°C or lower and a relative humidity of 30 percent or higher, and a subsequent main baking step in which heating is conducted at 200°C or higher at a relative humidity of 30 percent or lower. In this fashion, silica that has been converted during the prebaking at 200°C or lower at which device characteristics are not compromised is rendered denser during the main baking at low relative humidity. Thus, overall, device characteristics are not lost due to the device being exposed to high temperature and high humidity, and a high-purity siliceous film affording good density as an insulating film or the like is obtained.

[0048] The relative humidity in the main baking step of the present invention can be lowered by conducting an adequate prebaking step, and is desirably 20 percent or lower,

preferably 10 percent or lower. It is also possible to conduct the main baking step at a relative humidity of essentially 0 percent. During prebaking, as a source of oxygen for replacing the nitrogen in the polysilazane with oxygen, a relative humidity of at least about that contained in air is necessary. Specifically, the relative humidity during prebaking is at least 30 percent, desirably 40 percent or greater. When a higher humidity than that of air is desired, humidification can be conducted. For example, conversion to silica can be promoted during prebaking under conditions of heating at 200°C or lower and humidification yielding a relative humidity of 70 percent or higher, desirably under conditions of heating at 150°C or lower and humidification yielding a relative humidity of 75 percent or higher, and preferably, under conditions of heating at 100°C or lower and humidification yielding a relative humidity of 80 percent or higher.

[0049]

[Embodiments]

Reference Example (Synthesis of perhydropolysilazane)

In a four-necked flask with an internal capacity of 2 liters were mounted a gas blowing pipe, a mechanical stirrer, and a Dewar condenser. The interior of the reaction vessel was backfilled with dry nitrogen, and 1,500

mL of dry pyridine was introduced into the four-necked flask and cooled with ice. When 100 g of dichlorosilane was added, a while solid adduct ($SiH_2Cl_2 \cdot 2C_5H_5N$) formed. The reaction mixture was cooled with ice and 70 g of ammonia was blown in while stirring. The dry nitrogen was then blown for 30 minutes into the liquid layer and the excess ammonia was removed.

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[0050] The product obtained was filtered under reduced pressure and under a dry nitrogen atmosphere employing a Buechner funnel, yielding 1,200 mL of filtrate. An evaporator was employed to distill off the pyridine, yielding 40 g of perhydropolysilazane. When the number average molecular weight of the perhydrosilazane obtained was measured by GPC (developing solution: $CDCl_3$), a value of 800 based on polystyrene conversion was obtained. The infrared (IR) absorption spectrum exhibited absorption by N-H at wave numbers (cm^{-1}) in the vicinity of 3350 and 1200; absorption by Si-H at 2170; and absorption by Si-N-Si at 1020 to 820. Fig. 1 shows the IR spectrum.

[0051] Embodiment 1 (5 percent DPP added)

To a 300 mL capacity glass beaker were added 20 g of the perhydropolysilazane synthesized in the above-described reference example and 50 g of dibutyl ether and a

polysilazane solution was prepared. Next, 1.0 g of 1,3-di-4-piperidylpropane (DPP) was mixed with 30 g of dibutyl ether and thoroughly stirred. This mixture was slowly added dropwise over 5 minutes to the above polysilazane solution while stirring well with a stirrer.

[0052] Measurement of the number average molecular weight of the polysilazane obtained by GPC based on polystyrene revealed a value of 860. The IR spectrum revealed polysilazane absorption, that is, absorption based on N-H at wave numbers (cm^{-1}) of 3370 and 1180; absorption by Si-H at 2170 and 840, absorption by Si-N-Si at 1060 to 800, and absorption by C-H at wave numbers (cm^{-1}) of 2800 to 3100. Fig. 2 shows the IR spectrum.

[0053] Embodiment 2 (1 percent DPP added)

To a 300 mL capacity glass beaker were added 20 g of the perhydropolysilazane synthesized in the above-described reference example and 50 g of dibutyl ether and a polysilazane solution was prepared. Next, 0.2 g of DPP was mixed with 30 g of dibutyl ether and thoroughly stirred. This mixture was slowly added dropwise over 5 minutes to the above polysilazane solution while stirring well with a stirrer.

[0054] Measurement of the number average molecular weight of the polysilazane obtained by GPC based on polystyrene

revealed a value of 810. The IR spectrum revealed polysilazane absorption, that is, absorption based on N-H at wave numbers (cm^{-1}) of 3370 and 1180; absorption by Si-H at 2170 and 830, and absorption by Si-N-Si at 1060 to 800. Fig. 3 shows the IR spectrum.

[0055] Embodiment 3 (5 percent 4,4'-trimethylenebis(1-methylpiperidine) added)

To a 300 mL capacity glass beaker were added 20 g of the perhydropolysilazane synthesized in the above-described reference example and 50 g of dibutyl ether and a polysilazane solution was prepared. Next, 1.0 g of 4,4'-trimethylenebis(1-methylpiperidine) was mixed with 30 g of dibutyl ether and thoroughly stirred. This mixture was slowly added dropwise over 5 minutes to the above polysilazane solution while stirring well with a stirrer.

[0056] Measurement of the number average molecular weight of the polysilazane obtained by GPC based on polystyrene revealed a value of 890. The IR spectrum revealed polysilazane absorption, that is, absorption based on N-H at wave numbers (cm^{-1}) of 3370 and 1180; absorption by Si-H at 2160 and 830; absorption by Si-N-Si at 1060 to 800; and adsorption by C-H at wave numbers (cm^{-1}) of 2700 to 3100. Fig. 4 shows the IR spectrum.

[0057] Embodiment 4 (5 percent diazabicyclo[2.2.2]octane added)

To a 300 mL capacity glass beaker were added 20 g of the perhydropolysilazane synthesized in the above-described reference example and 50 g of dibutyl ether and a polysilazane solution was prepared. Next, 1.0 g of diazabicyclo[2.2.2]octane was mixed with 30 g of dibutyl ether and thoroughly stirred. This mixture was slowly added dropwise over 5 minutes to the above polysilazane solution while stirring well with a stirrer.

[0058] Measurement of the number average molecular weight of the polysilazane obtained by GPC based on polystyrene revealed a value of 950. The IR spectrum revealed polysilazane absorption, that is, absorption based on N-H at wave numbers (cm^{-1}) of 3370 and 1180; absorption by Si-H at 2170 and 830; absorption by Si-N-Si at 1060 to 800; and adsorption by C-H at wave numbers (cm^{-1}) of 2800 to 3000. Fig. 5 shows the IR spectrum.

[0059] Embodiment 5 (5 percent cis-2,6-dimethylpiperazine added)

To a 300 mL capacity glass beaker were added 20 g of the perhydropolysilazane synthesized in the above-described reference example and 50 g of dibutyl ether and a polysilazane solution was prepared. Next, 1.0 g of cis-

2,6-dimethylpiperazine was mixed with 30 g of dibutyl ether and thoroughly stirred. This mixture was slowly added dropwise over 5 minutes to the above polysilazane solution while stirring well with a stirrer.

[0060] Measurement of the number average molecular weight of the polysilazane obtained by GPC based on polystyrene revealed a value of 950. The IR spectrum revealed polysilazane absorption, that is, absorption based on N-H at wave numbers (cm^{-1}) of 3370 and 1180; absorption by Si-H at 2170 and 830; and absorption by Si-N-Si at 1060 to 800. Fig. 6 shows the IR spectrum.

[0061] <u>Comparative Example (5 percent tripentylamine added)</u>

To a 300 mL capacity glass beaker were added 20 g of the perhydropolysilazane synthesized in the above-described reference example and 50 g of dibutyl ether and a polysilazane solution was prepared. Next, 1.0 g of tripentylamine was mixed with 30 g of dibutyl ether and thoroughly stirred. This mixture was slowly added dropwise over 5 minutes to the above polysilazane solution while stirring well with a stirrer.

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[0062] Measurement of the number average molecular weight of the polysilazane obtained by GPC based on polystyrene revealed a value of 860. The IR spectrum revealed

polysilazane absorption, that is, absorption based on N-H at wave numbers (cm^{-1}) of 3300 and 1180; absorption by Si-H at 2170 and 830; absorption by Si-N-Si at 1060 to 800; and absorption by C-H at wave numbers (cm^{-1}) of 2800 to 3000. Fig. 13 shows the IR spectrum.

[0063] <u>Conversion to silica and physical properties of the siliceous film</u>

The perhydrosilazane of the reference example and the polysilazane-containing compositions of the present invention obtained in Embodiments 1 to 5 were converted to siliceous films by the following methods and the physical properties of the films were examined.

<u>Film formation and conversion to silica</u>

The perhydrosilazane and the polysilazane-containing compositions of the present invention were separately dissolved in dibutyl ether to prepare 20 percent solutions. The solutions were applied by spin coating (2,000 rpm, 20 s) on silicon wafers 10.16 cm (4 inches) in diameter and 0.5 mm in thickness. The coatings obtained were converted to silica under the following three sets of conditions:

(1) Being maintained for 10 seconds in a thermo-hygrostat at 90°C and 80 percent relative humidity;

(2) Being maintained for 3 minutes on a hot plate at 200°C in air (relative humidity 40 percent), and then baked at 400°C in dry air (relative humidity 0 percent); and

(3) Being left standing for 3 days in air (25°C, 40 percent relative humidity).

[0064] Rate of conversion to silica

The rate of conversion to silica was determined qualitatively from the IR spectrum. The results were denoted as follows: ◎: essentially complete conversion; ○: nearly complete conversion; and X: incomplete conversion.

[0065] Film density

A silicon wafer 10.16 cm (4 inches) in diameter and 0.5 mm in thickness was weighed with an electronic scale. A coating of polysilazane solution or the polysilazane-containing composition of the present invention was applied to the wafer by the above-described spin coating method. The coating was converted to silica and the wafer with the siliceous film was weighed again with the electronic scale. The weight of the film was calculated as the difference in weight before and after film formation. The film thickness was measured with a contact needle-type film thickness measuring apparatus (Dektak 11A, made by Sloan). The density was calculated by the following equation:

Film density (g/cm^3) = film weight (g)/film thickness (μm)/0.008

[0066] Etching rate (density property)

Following conversion to silica, the silicon wafer was immersed in 5 percent buffered hydrofluoric acid and the time required for removal of the film was measured. The corrosion rate per minute (Å/min) was obtained from the film thickness as measured by the contact needle-type film thickness measuring apparatus and the time required for removal of the film.

[0067] Smoke

In above-described silica conversion conditions (2), visual observation was made as to whether or not smoke was present immediately after placement on a 200°C hot plate. Data on the physical properties of the various films above were recorded in the following table.

[0068]

[Table 1]

Table 1 Comparison of film physical properties and the like

	Silica conversion conditions (1)			Silica conversion conditions (2)				Silica conversion conditions (3)		
	Rate of conversion to	Film density	Etching rate	Rate of conversion to	Film density	Etching rate	Smoking	Rate of conversion to	Film density	Etching rate

	silica			silica				silica		
		(g/cc)	(Å/min)		(g/cc)	(Å/min)			(g/cc)	(Å/min)
Ref. Ex.	X (Fig. 7)	1.4	>10,000	X (Fig. 8)	1.8	>10,000	Large amount	X (Fig. 9)	1.4	>10,000
Emb. 1	◎ (Fig. 10)	2.1	4800	◎ (Fig. 11)	2.3	3000	None	○ (Fig. 12)	1.9	5000
Emb. 2	◎	2.0	4900	◎	2.1	4300	None	○	1.9	5200
Emb. 3	◎	2.1	3800	◎	2.1	3400	None	○	2.0	4100
Emb. 4	◎	2.0	5000	◎	2.3	2700	None	○	1.9	5000
Emb. 5	◎	1.9	5200	◎	2.2	3000	None	○	1.8	5300
Comp. Ex.	△	1.7	>10,000	△	1.9	>10,000		△	1.7	>10,000

[0069] From Table 1, it will be understood that the polysilazane compositions (Embodiments 1 to 5) containing an N-heterocyclic compound of the present invention underwent essentially complete conversion to silica under all of conditions (1) to (3) above. However, the polysilazane composition (reference example) that did not contain an N-heterocyclic compound stopped before undergoing complete conversion under the above conditions. Further, the polysilazane compositions (Embodiments 1 to 5) containing an N-heterocyclic compound of the present invention exhibited better rates of conversion to silicon,

film densities, and density properties than the polysilazane composition (comparative example) that contained an aliphatic amine in the form of tripentylamine. Since the polysilazane composition containing an N-heterocyclic compound of the present invention converted to a siliceous film under all conversion conditions, it was found to present the possibility of a variety of use methods based on the type of material being coated and the desired application. Further, the smoke test under silica conversion conditions (2) revealed that in the polysilazane composition containing an N-heterocyclic compound of the present invention, the low-molecular-weight components of the polysilazane did not vaporize and scatter during heating.

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[0070] Embodiment 6

The perhydrosilazane synthesized in the reference example was dissolved in m-xylene and a 12 weight percent polysilazane solution was prepared. While stirring this solution, 4,4'-trimethylenebis(1-methylpiperidine) was gradually added at room temperature to 3 weight percent. The solution was coated by the gravure (reverse) coating method (roll #80) on one side of a polyethylene terephthalate (PET) film base material measuring 75 μm in

thickness, 60 cm in width, and 300 m in total extension while conveying the base material at 5 m/min. Next, the coating was passed through a solvent drying zone (80°C, internal conveyance distance of 10 m) at the above conveying rate to dry the polysilazane coating (retention time of 2 minutes). The polysilazane coated film that had passed through the drying zone was conveyed at the above conveying rate through a humidifying furnace with an internal conveying distance of 10 m that was maintained at a temperature of 95°C and a relative humidity of 80 percent to expose the polysilazane coating to a steam atmosphere for 10 minutes.

[0071] Evaluation of film characteristics

The ceramic coating obtained in Embodiment 6 was confirmed to have been essentially completely converted to silica by the disappearance of the Si-H oscillation (N-H oscillation) peak and the appearance of an Si-O oscillation peak by the IR spectral method. The thickness of the ceramic coating was found to be consistently 0.6 μm as calculated from the peaks generated by interference in visible range spectra by the spectral method.

[0072] The ceramic coating was evaluated for the various characteristics given below. For reference, the

characteristics of the plastic film base material employed, other than adhesion (5), were measured.

(1) Oxygen permeability(unit: $cc/m^2/24$ h/atm)

Measurement was conducted at 25°C and 65 percent RH with a measuring apparatus made by Mokon.

(2) Steam permeability (unit: $g/m^2/24$ h)

Measurement was conducted at 40°C with a Mokon measuring apparatus.

(3) Light transmittance

The average transmittance of visible light was measured with a haze meter.

(4) Scratch resistance

Testing was conducted with #000 steel wool under conditions of a load of 250 g and 100 rotations (60 rpm). The number of scratches was visually determined and evaluated on a scale of A to E. Evaluation of A: no scratching; evaluation of B: not more than 2 scratches; evaluation of C: 3 to 5 scratches; evaluation of D: 6 to 10 scratches; and evaluation of E: 11 or more scratches.

(5) Adhesion

Evaluated by a checkerboard tape peeling test.

[0073]

Table 2

	Film base material	Film with siliceous coating
Oxygen permeability	25	1.5
Steam permeability	12	1.9
Light transmittance	88	91
Scratching resistance	E	B
Adhesion		100/100

[0074] Table 2 reveals that use of the polysilazane composition of the present invention imparted good gas barrier properties to a transparent film base material.

[0075]

[Effect of the Invention] Adding an N-heterocyclic compound to a polysilazane composition based on the present invention greatly increases the rate of conversion to silica relative to the use of polysilazane alone or conventional polysilazane compositions, and permits the conversion of a polysilazane thin film to a siliceous film under ambient conditions of low relative humidity, and in some cases, even in a dry atmosphere. Thus, when applying polysilazane-derived siliceous films to the insulating

films, smoothing films, and the like of semiconductor devices and liquid-crystal devices, it is possible to avoid high-temperature and highly humid atmospheres that risk negatively affecting device characteristics. Further, an increase in the rate of conversion to silica increases the ratio of high-molecular-weight conversion of low-molecular-weight components of polysilazane prior to reaching their boiling points and prevents them from vaporizing during heating. Thus, the vaporization of low-molecular-weight components is reduced in the course of heating polysilazane thin films, contamination of the heating apparatus and the like is prevented, and the amount of scattering vapor is reduced, thereby increasing the yield of siliceous film.

[Brief Description of Drawings]

[Fig. 1] An IR spectrum of the perhydrosilazane obtained for the reference example.

[Fig. 2] An IR spectrum of the perhydrosilazane composition obtained for Embodiment 1.

[Fig. 3] An IR spectrum of the perhydrosilazane composition obtained for Embodiment 2.

[Fig. 4] An IR spectrum of the perhydrosilazane composition obtained for Embodiment 3.

[Fig. 5] An IR spectrum of the perhydrosilazane composition obtained for Embodiment 4.

[Fig. 6] An IR spectrum of the perhydrosilazane composition obtained for Embodiment 5.

[Fig. 7] An IR spectrum after conversion to silica of the perhydropolysilazane obtained in the reference example under silica conversion conditions (1).

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[Fig. 8] An IR spectrum after conversion to silica of the perhydropolysilazane obtained in the reference example under silica conversion conditions (2).

[Fig. 9] An IR spectrum after conversion to silica of the perhydropolysilazane obtained in the reference example under silica conversion conditions (3).

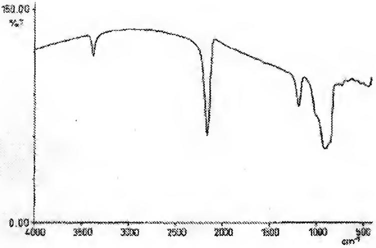
[Fig. 10] An IR spectrum after conversion to silica of the polysilazane-containing composition obtained in Embodiment 1 under silica conversion conditions (1).

[Fig. 11] An IR spectrum after conversion to silica of the polysilazane-containing composition obtained in Embodiment 1 under silica conversion conditions (2).

[Fig. 12] An IR spectrum after conversion to silica of the polysilazane-containing composition obtained in Embodiment 1 under silica conversion conditions (3).

[Fig. 13] An IR spectrum of the polysilazane-containing composition obtained in the comparative example.

Fig. 1



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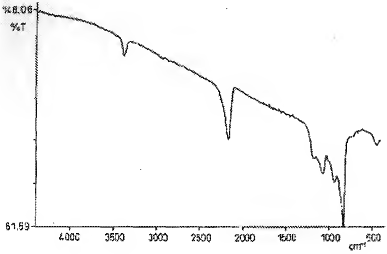

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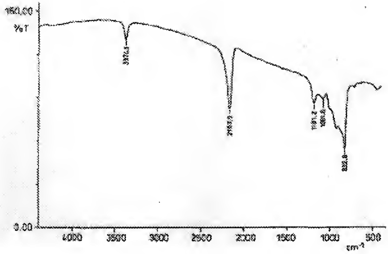
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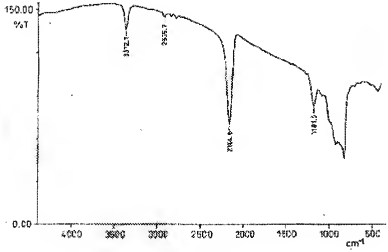
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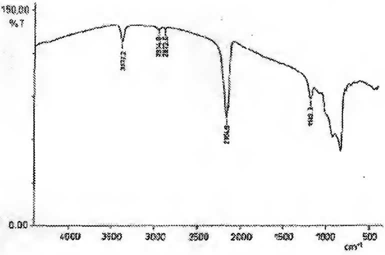
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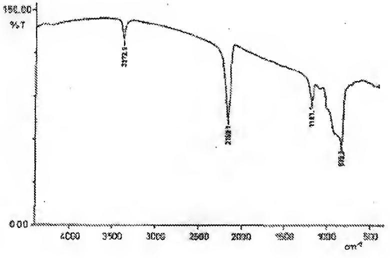
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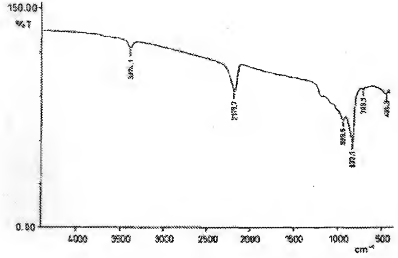
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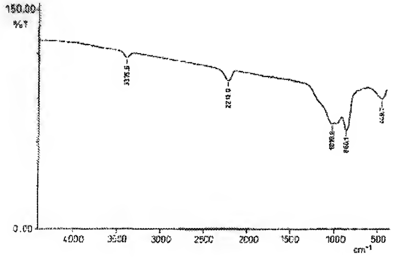
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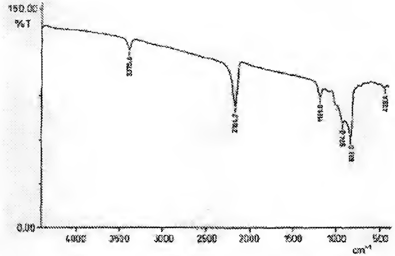
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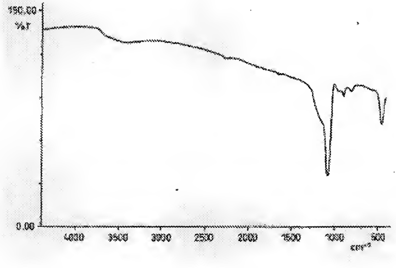
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Fig. 11

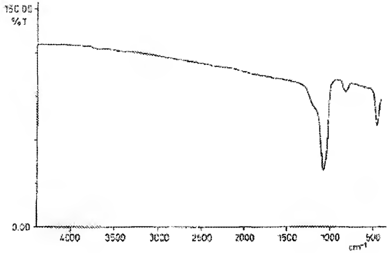
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Fig. 12

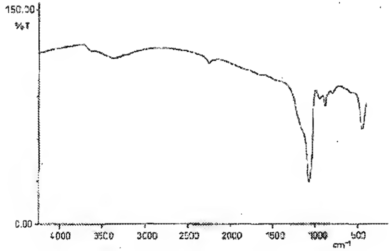
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Fig. 13